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Two Heteropoly Anions Containing Organic Groups. The Crystal and Molecular Structures of Ammonium Pentamolybdobis(methylphosphonate)Pentahydrate, ~~$(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$~~ and Sodium Tetramethylammonium Pentamolybdobis(ethylammoniumphosphonate)Pentahydrate. ~~$Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$~~

by

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Abstract

The crystal and molecular structures of two stable organic derivatives of a heteropoly anion have been determined from three-dimensional X-ray data collected by counter methods. The pentamolybdomethylphosphonate compound, $(NH_4)_4$-$[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$, crystallizes in space group C_2^2-$P2_1$ of the monoclinic system with four formula units in a cell of dimensions a=10.597(2), b=13.739(2), c=19.901(2)Å; β=96.05(1)°. The observed and calculated densities are 2.48(2) and 2.466 g/cm^3, respectively. The pentamolybdoethylammoniumphosphonate compound, $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$, crystallizes in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four formula units in a cell of dimensions a=11.513(4), b=20.146(6), c=14.110(5)Å; β=95.25(4)°. The observed and calculated densities are 2.36(2) and 2.354 g/cm^3, respectively. Both structures have been refined by least-squares techniques to final R factors on F of 0.032 for the methyl compound and 0.047 for the ethylammonium compound. The structures of both organoheteropoly anions are similar, consisting of rings of five MoO_6 octahedra joined by sharing edges, except for one pair which is joined by corner-sharing. Each face of the Mo_5 ring is capped by a tetrahedral RPO_3 group ($R=CH_3$ or $C_2H_4NH_3^+$). The crystal structure of the methyl compound contains two independent $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions of the same chirality related by a pseudo-symmetric B-centering. The ammonium ions and water molecules form infinite hydrogen-bonded chains parallel to the b axis. In the ethylammonium crystal the $[(NH_3C_2H_5P)_2Mo_5O_{21}]^{2-}$ anions are loosely linked together as dimers by sodium ion - oxygen coordination. This is the first example of a zwitterionic heteropoly anion.

Introduction

Kwak, Pope, and Scully[1] have recently reported the synthesis and characterization of several salts of the anions $[(RP)_2Mo_5O_{21}]^{4-}$, where R=H, CH_3, C_2H_5, C_6H_5, $C_2H_4NH_3^+$, and p-$CH_2C_6H_4NH_3^+$. These are the first heteropoly anions in which organic groups are covalently bonded to a phosphorus heteroatom. It seems probable that they represent a large class of compounds which may include a wide variety of anion types, heteroatoms, and organic moieties.[2] This combination of the unusual properties of heteropoly anions with the chemical versatility of organic functional groups is expected to produce new species with interesting chemical and physical properties, involving in some cases entirely new structural types.

The X-ray crystal structure determinations of two of these organophosphonate complexes, $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I) and $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot5H_2O$ (II) were undertaken to confirm the presence of the organic moieties in the heteropoly anions and to determine the effect of these organic substituents on the geometry of the anions. Knowledge of the structures of these complexes should help to provide information on the geometric requirements for the formation of new organoheteropoly anions.

Experimental Section

$(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot5H_2O$ (I). Unit Cell and Space Group. Crystals of I were kindly supplied by Professor M.T. Pope. A well-formed, colorless prism approximately 0.3 mm on an edge was mounted on a glass fiber with the $[\bar{1}01]$ direction coincident with the goniometer rotation axis. Preliminary Weissenberg and precession photographs exhibited monoclinic symmetry with systematic absences for 0k0, $k \neq 2n$, indicating possible space groups C_2^2-$P2_1$ or C_{2h}^2-$P2_1/m$. The cell dimensions, a=10.597(2), b=13.739(2), c=19.901(2)Å, β=96.05(1)°, were obtained using $MoK\alpha_1$ radiation (λ=0.70926Å) at 22°C by a least-squares refinement to fit the ±2θ values for 19 high-angle reflections centered on the *Picker FACS-I four-circle* diffractometer. The observed density of 2.48(2) g/cm³ obtained by flotation in CCl_4-$C_2H_2Br_4$ solutions agrees well with the calculated value of 2.466 g/cm³ assuming Z=4.

Collection and Reduction of Intensity Data. The same crystal used for unit cell determination was used for data collection. Diffractometer data were obtained using Zr-filtered MoKα radiation by the θ-2θ scan technique at a take-off angle of 1.5°. The peaks were scanned at a rate of 1.0°/min from 0.5° on the low-angle side of the $K\alpha_1$ peak to 0.5° on the high-angle side of the $K\alpha_2$ peak. The diffracted beams were counted using a scintillation counter and were attenuated with zirconium foil whenever the count rate exceeded 8000 cps. Stationary-crystal, stationary-counter background counts of 10

sec were taken at each end of the scan.

A unique data set was collected to $2\theta = 50°$. The intensities of three reflections were monitored as standards every 100 reflections, and no loss in intensity was observed throughout the data collection. The intensities were corrected for background and standard deviations were assigned according to the equations $I = C - 0.5(t_c/t_b)(B_1+B_2)$ and $\sigma(I) = [C + 0.25(t_c/t_b)^2(B_1+B_2) + (pI)^2]^{\frac{1}{2}}$ where C is the integrated peak count obtained in time t_c and B_1 and B_2 are the background counts obtained in time t_b, all corrected for scalar truncation. A value of 0.06 was used for p. The data were also corrected for Lorentz and polarization effects. No absorption correction was applied; the linear absorption coefficient of 22.9 cm^{-1} was calculated to give transmission coefficients ranging from 0.5 to 0.3. Of the 5332 unique data collected, only the 4864 reflections for which *$I \geq 2\sigma(I)$ were used in the structure solution and refinement.*

Solution and Refinement of the Structure. A Patterson function was computed[3] which clearly indicated (1) the correct choice of space group is $P2_1$, and (2) the two independent molecules in the unit cell are almost exactly separated by a pseudo B-centering translation of $\frac{1}{2}, 0, \frac{1}{2}$. This pseudo-symmetry results in an apparent 2_1 axis at

$\frac{1}{4}, 0, \frac{1}{4}$ which was originally (incorrectly) chosen as the cell origin. However, even with a correct choice of origin a model consisting of two identical rings each containing five Mo atoms failed to refine satisfactorily. A careful re-examination of the Patterson map revealed a slight elongation in the w-direction of one peak on the Harker plane at $v=\frac{1}{2}$, indicating a breaking of the pseudo-symmetry in the z-direction for one pair of Mo atoms. Fortunately, a model assuming exact B-centering except for this one z-coordinate refined in 7 cycles to give a reasonable geometry for both five-molybdenum rings. The asymmetric ring of anion I (see below) is rotated from that of anion I', breaking the pseudo-symmetry. *The y-coordinate of Mo(1) was fixed* at 0.25 to define the origin of the unit cell, and *an isotropic thermal parameter of 1.5Å² was assumed for each* of the 10 Mo atoms. The consistency indices R_1 and R_2 were 0.25 and 0.35, respectively, where $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)^{\frac{1}{2}}$. In this and succeeding refinements the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$.

Two subsequent difference Fourier maps, interspersed with a least-squares refinement, led to the positions of all re-

maining non-hydrogen atoms. Four cycles of refinement assuming individual isotropic thermal parameters for all atoms led to values of 0.052 and 0.064 for R_1 and R_2. The atomic scattering factors used were those of Hanson et al.[4], while the values of the anomalous terms $\Delta f'$ and $\Delta f''$ were taken from Cromer.[5]

At this point in the solution of the structure a refinement with all x, y, z fractional coordinates converted to $\bar{x}$, $\bar{y}$, $\bar{z}$ failed to determine the polarity of the crystal, refining to essentially identical consistency indices. Hence 12 reflections were selected which calculations indicated should show the greatest differences between $F(hk\ell)$ and $F(\bar{h}\bar{k}\bar{\ell})$. Using the same conditions as described above for data collection, the intensities of the $(hk\ell)$, $(h\bar{k}\ell)$, $(\bar{h}\bar{k}\bar{\ell})$, and $(\bar{h}k\bar{\ell})$ reflections were re-collected and processed as before, averaging the intensities of $(hk\ell)$ with $(\bar{h}k\bar{\ell})$. In each case, the observed inequality between $F(hk\ell)$ and $F(\bar{h}\bar{k}\bar{\ell})$ was in the same direction as the calculated inequality (Table I), consistent with a correct initial choice of crystal polarity.

In hopes of differentiating between the eight NH_4^+ cations and the 10 water molecules, one cycle of anisotropic refinement, varying first three blocks of anisotropic thermal parameters followed by positional refinement of the 78 non-hydrogen atoms, was carried out. A difference Fourier map gave some indications of hydrogen positions; these peaks, together with an

TABLE I

Determination of Polarity of a Crystal of

$(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$ (I)

Indices			F_{obs}		F_{calc}[a]	
h	k	ℓ	$hk\ell$	$\bar{h}\bar{k}\bar{\ell}$	$hk\ell$	$\bar{h}\bar{k}\bar{\ell}$
$\bar{2}$	5	2	62	54	74	65
3	4	3	35	41	32	37
0	5	4	83	92	68	79
$\bar{1}$	4	5	68	75	55	61
$\bar{1}$	1	7	42	37	46	41
$\bar{3}$	4	5	99	91	104	95
$\bar{3}$	1	5	64	70	66	71
4	3	0	93	88	97	91
7	3	7	56	51	59	54
1	4	6	37	34	39	35
$\bar{4}$	2	6	75	73	79	74
5	5	7	34	38	28	32

[a]Based on final structure parameters.

assumed NH_4^+ - NH_4^+ contact distance of about 4Å, resulted in the probable assignment reported. A final cycle of anisotropic refinement, in which no parameter shifted by more than its standard deviation, gave final values of R_1=0.032 and R_2=0.042, with a standard deviation in an observation of unit weight of 1.07. A difference Fourier map showed no peak greater than 0.7e/Å^3, compared to an average value for oxygen of 5.0e/Å^3.

Table II presents the positional and thermal parameters, along with the corresponding standard deviations. A table of the final values of $|F_o|$ and $|F_c|$ is available.[6]

Na[N(CH$_3$)$_4$][(NH$_3$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$]·5H$_2$O (II). Unit Cell and Space Group. Colorless crystals of II were supplied by Professor M.T. Pope. A crystal of approximate dimensions 0.2 x 0.3 x 0.3 mm was mounted parallel to the [100] direction and exhibited monoclinic symmetry in precession photographs. Systematic absences on the hk0, h0ℓ, and h1ℓ nets for 0k0, k≠2n, and h0ℓ, ℓ≠2n, uniquely established the space group as C_{2h}^5-$P2_1/c$. The cell dimensions, obtained using MoKα radiation (λ=0.71069 Å) by centering 22 reflections at ±2θ on the Picker FACS-I four-circle diffractometer, are a=11.513(4), b=20.146(6), c=14.110(5)Å; β=95.25(4)° (t=22°). The calculated density of 2.354 g/cm^3 for four formula units in the unit cell agrees well with the experimental value of 2.36(2) g/cm^3 obtained by flotation in CCl_4-$C_2H_2Br_4$ solutions.

Collection and Reduction of Intensity Data. The crystal used for unit cell determination was also used for data collec-

TABLE II

Final Positional and Thermal Parameters for $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$ (I)

Atom	Fractional coordinates: x	y	z	Anisotropic temperature factors ($\times10^4$)[a]: β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	1.09494(7)[b]	0.25	0.63626(4)	39.4(7)	15.7(4)	9.6(2)	4.5(4)	0.7(3)	-2.0(2)
Mo(2)	1.23246(7)	0.45577(8)	0.73854(4)	36.3(7)	23.6(5)	9.4(2)	2.3(5)	-1.2(3)	-2.7(3)
Mo(3)	0.99310(7)	0.61630(8)	0.74526(4)	43.3(7)	14.8(4)	10.1(2)	1.6(4)	1.1(3)	-2.6(3)
Mo(4)	0.75471(7)	0.55058(8)	0.62870(4)	40.5(7)	16.7(4)	11.9(2)	6.3(5)	-2.2(3)	-0.8(3)
Mo(5)	0.82475(7)	0.33892(8)	0.55291(4)	43.1(7)	18.1(4)	9.5(2)	2.4(5)	-4.2(3)	-2.9(3)
Mo(1')[c]	0.22694(7)	0.55228(8)	0.13609(4)	31.1(6)	15.6(4)	12.3(2)	2.6(5)	0.7(3)	0.0(3)
Mo(2')	0.32180(7)	0.33176(8)	0.04651(4)	35.6(7)	15.4(4)	10.4(2)	-1.1(4)	-2.3(3)	-1.4(2)
Mo(3')	0.59607(7)	0.25719(8)	0.13500(4)	36.1(7)	14.6(4)	11.5(2)	3.1(4)	-1.0(3)	0.9(2)
Mo(4')	0.70493(7)	0.44282(8)	0.23453(4)	32.5(6)	17.0(4)	9.9(2)	-0.2(5)	-0.7(3)	-0.4(2)
Mo(5')	0.49632(7)	0.63036(8)	0.22548(4)	38.7(7)	15.3(4)	10.6(2)	0.1(4)	0.2(3)	-1.9(3)
P(1)	1.0632(2)	0.5053(2)	0.5936(1)	42.4(21)	16.0(12)	7.6(6)	-1.2(13)	1.9(9)	0.9(7)
P(2)	0.9057(2)	0.3736(2)	0.7290(1)	35.3(20)	15.9(12)	8.9(6)	-0.6(13)	2.1(9)	-0.2(7)
P(1')	0.5373(2)	0.5022(2)	0.0824(1)	34.9(19)	15.9(12)	7.5(5)	-1.6(13)	2.6(8)	1.3(7)
P(2')	0.3882(2)	0.3827(2)	0.2253(1)	39.0(21)	18.1(13)	9.2(6)	-0.7(13)	2.9(9)	2.7(7)
O(1)	1.1860(6)	0.2453(5)	0.5696(3)	54(6)	32(4)	16(2)	8(4)	6(3)	-7(2)
O(2)	1.1207(6)	0.1385(5)	0.6713(3)	72(7)	22(4)	22(2)	17(4)	7(3)	1(2)
O(3)	1.2040(5)	0.3325(5)	0.6939(3)	42(6)	33(4)	12(2)	5(4)	-3(2)	0(2)
O(4)	0.9715(5)	0.2779(4)	0.7200(3)	52(6)	14(3)	12(2)	3(4)	7(3)	4(2)
O(5)	0.9258(6)	0.2322(4)	0.5917(3)	68(6)	18(3)	9(1)	4(4)	1(2)	-3(2)
O(6)	1.0144(6)	0.3982(4)	0.5866(3)	52(6)	21(4)	11(2)	-3(4)	-1(3)	-2(2)
O(7)	1.0051(5)	0.4535(5)	0.7438(3)	45(5)	23(4)	11(2)	0(4)	0(2)	1(2)
O(8)	1.1953(5)	0.5066(5)	0.6312(3)	50(6)	23(4)	13(2)	-7(4)	3(3)	-3(2)
O(9)	1.3870(6)	0.4755(5)	0.7309(3)	55(6)	37(4)	15(2)	-2(4)	2(3)	-5(2)
O(10)	1.2374(6)	0.4186(5)	0.8220(3)	56(6)	41(4)	11(2)	7(4)	-4(3)	0(2)
O(11)	1.1695(6)	0.5858(5)	0.7468(3)	41(6)	25(4)	15(2)	-9(4)	2(3)	-6(2)
O(12)	0.9821(6)	0.6270(5)	0.9305(3)	64(6)	32(4)	17(2)	0(4)	4(3)	3(3)
O(13)	0.9721(6)	0.5680(5)	0.6304(3)	54(6)	22(3)	11(2)	-2(4)	4(3)	-2(2)
O(14)	0.8158(6)	0.5866(5)	0.7191(3)	45(6)	27(4)	13(2)	4(4)	3(3)	-3(2)
O(15)	0.9979(7)	0.7350(5)	0.7185(4)	84(8)	22(4)	19(2)	-1(5)	2(3)	3(2)
O(16)	0.6015(6)	0.5200(6)	0.6379(4)	46(6)	45(5)	24(2)	4(4)	0(3)	-4(3)
O(17)	0.8163(5)	0.3981(4)	0.6650(3)	52(6)	18(4)	7(2)	3(4)	1(2)	1(2)
O(18)	0.7811(6)	0.4756(5)	0.5489(3)	70(6)	17(3)	11(2)	11(4)	-7(3)	2(2)
O(19)	0.7390(7)	0.6627(5)	0.5890(3)	86(7)	20(4)	20(2)	11(4)	-3(3)	4(2)
O(20)	0.8490(7)	0.3246(5)	0.4701(3)	109(8)	37(5)	13(2)	6(5)	1(3)	-3(2)
O(21)	0.6801(6)	0.2888(5)	0.5594(4)	55(6)	25(4)	23(2)	-1(4)	-6(3)	-1(2)
O(1')	0.2196(6)	0.6395(5)	0.0740(3)	58(7)	32(4)	17(2)	6(4)	-1(3)	7(2)
O(2')	0.0766(6)	0.5536(5)	0.1578(3)	48(6)	33(4)	23(2)	8(4)	7(3)	0(3)
O(3')	0.2303(5)	0.4410(5)	0.0775(3)	32(5)	19(3)	18(2)	3(4)	-5(2)	-1(2)
O(4')	0.2604(5)	0.4334(5)	0.2124(3)	47(5)	27(4)	10(2)	0(3)	7(2)	2(2)
O(5')	0.3131(5)	0.6224(5)	0.2108(3)	41(5)	23(4)	12(2)	4(4)	2(2)	1(2)
O(6')	0.4510(5)	0.5564(5)	0.1277(3)	34(5)	19(3)	11(2)	-3(4)	-3(2)	1(2)
O(7')	0.4180(5)	0.3274(4)	0.1605(3)	47(6)	17(3)	13(2)	-4(4)	-2(2)	2(2)
O(8')	0.4532(5)	0.4536(5)	0.0242(3)	49(5)	25(4)	9(2)	-13(4)	2(2)	0(2)
O(9')	0.2785(6)	0.3332(5)	-0.0381(3)	53(6)	39(4)	15(2)	-5(4)	-6(3)	-5(2)
O(10')	0.2270(6)	0.2411(5)	0.0727(3)	54(7)	25(4)	18(2)	-4(4)	1(3)	2(2)
O(11')	0.4829(6)	0.2659(5)	0.0516(3)	48(6)	25(4)	13(2)	8(4)	-2(3)	-5(2)
O(12')	0.5602(7)	0.1429(5)	0.1587(4)	84(7)	15(4)	25(2)	-7(4)	-7(3)	5(2)
O(13')	0.6212(5)	0.4278(5)	0.1235(3)	38(5)	20(3)	12(2)	-4(4)	-2(2)	2(2)
O(14')	0.6573(5)	0.3081(4)	0.2238(3)	41(6)	20(3)	14(2)	3(4)	-6(2)	2(2)
O(15')	0.7350(6)	0.2419(5)	0.0997(3)	48(6)	44(4)	15(2)	3(4)	0(3)	-6(2)
O(16')	0.7387(6)	0.4401(5)	0.3211(3)	86(7)	32(4)	10(2)	1(5)	-7(3)	1(2)
O(17')	0.4931(5)	0.4555(5)	0.2475(3)	44(5)	21(3)	10(1)	-5(4)	3(2)	0(2)
O(18')	0.6626(5)	0.5758(4)	0.2157(3)	37(5)	20(3)	15(2)	-3(3)	4(3)	3(2)
O(19')	0.8532(6)	0.4440(5)	0.2071(3)	58(6)	35(4)	15(2)	-2(4)	4(3)	-2(2)
O(20')	0.5212(6)	0.7417(5)	0.1951(4)	73(7)	21(4)	26(2)	-10(4)	-3(3)	3(2)
O(21')	0.5099(6)	0.6488(6)	0.3127(3)	73(7)	41(6)	17(2)	6(5)	-1(3)	-9(2)
C(1)	1.0643(10)	0.5517(8)	0.5097(5)	95(11)	32(6)	13(3)	-16(7)	1(5)	6(4)
C(2)	0.8142(10)	0.3630(7)	0.7989(5)	92(11)	20(5)	15(2)	3(6)	21(4)	1(3)
C(1')	0.6405(10)	0.5892(8)	0.0481(5)	75(10)	30(6)	19(3)	-19(6)	0(4)	8(3)
C(2')	0.3788(9)	0.2954(8)	0.2921(5)	67(10)	37(6)	14(3)	-3(6)	9(4)	11(3)
N(1)	0.0636(9)	0.4472(7)	0.3097(5)	113(11)	30(5)	29(3)	-3(7)	-7(5)	-1(4)
N(2)	0.4527(9)	0.3445(7)	0.6244(5)	112(11)	30(5)	27(3)	-6(6)	25(5)	-8(3)
N(3)	0.6778(8)	0.5625(7)	0.4292(4)	72(8)	44(6)	14(2)	-4(6)	3(4)	4(3)
N(4)	0.2704(9)	0.7152(7)	0.6485(4)	98(10)	35(5)	18(2)	-26(6)	-4(4)	2(3)
N(5)	0.5063(8)	0.4398(7)	-0.1210(4)	85(9)	36(6)	21(3)	-1(6)	-4(4)	4(3)
N(6)	1.0049(8)	0.3310(7)	0.1266(5)	59(8)	35(5)	29(3)	-9(6)	19(4)	-3(3)
N(7)	1.1931(10)	0.5465(7)	-0.0661(5)	145(11)	34(6)	17(2)	0(7)	10(4)	-2(3)
N(8)	0.8496(9)	0.7072(7)	0.1769(5)	88(10)	42(6)	22(3)	-31(6)	6(4)	-11(3)
Aq(1)	0.1161(8)	0.3304(6)	0.4283(4)	150(10)	44(5)	24(2)	24(6)	19(4)	5(3)
Aq(2)	0.3879(9)	0.3666(9)	0.4843(5)	138(12)	90(8)	34(3)	-1(8)	-9(5)	6(4)
Aq(3)	0.4110(7)	0.5631(7)	0.4478(4)	73(8)	76(7)	32(3)	7(6)	6(4)	10(4)
Aq(4)	0.2249(6)	0.6026(6)	0.3419(4)	54(7)	52(5)	29(2)	-5(5)	12(3)	-16(3)
Aq(5)	0.4633(8)	0.6979(7)	0.5611(4)	94(8)	59(5)	23(2)	27(5)	-3(4)	-7(3)
Aq(6)	0.6453(8)	0.3028(7)	-0.0470(4)	131(10)	57(6)	24(2)	42(6)	11(4)	10(3)
Aq(7)	0.8972(10)	0.3479(10)	-0.0097(5)	156(13)	106(9)	34(3)	-8(9)	15(5)	16(5)
Aq(8)	0.9383(9)	0.5373(9)	-0.0411(5)	149(12)	104(9)	37(3)	-11(9)	27(5)	4(5)
Aq(9)	0.7096(8)	0.5705(6)	-0.1503(5)	101(9)	37(5)	48(3)	-16(5)	29(5)	-7(3)
Aq(10)	0.9497(8)	0.6966(8)	0.0510(4)	98(8)	75(6)	31(3)	38(6)	10(4)	12(3)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

[b] Numbers in parentheses in this and succeeding tables are estimated standard deviations in the least significant figures.

[c] The primed atoms comprise the second anion (I'), and are chemically equivalent to the unprimed atoms of the same number in the first anion (I).

tion. A unique data set to $2\theta=45°$ was collected using the same conditions as described for **I**, with the exception that the peaks were scanned from 0.75° below the $K\alpha_1$ peak to 0.75° above the $K\alpha_2$ peak. The intensities of three standard reflections, monitored every 100 reflections, remained essentially constant during data collection. The intensities were corrected for background and for Lorentz and polarization effects as described for **I**. No absorption correction was applied; the linear absorption coefficient of 20.5 cm^{-1} was estimated to give transmission coefficients ranging from 0.6 to 0.4. Of the 4279 reflections processed, 3541 were considered to be observed ($I\geq 2\sigma(I)$) and were used in the solution and refinement of the structure.

Solution and Refinement of the Structure. Normalized structure factors were calculated, and the multiple-solution symbolic addition technique was applied utilizing the LSAM series of computer programs. 395 reflections were selected for which $E\geq 1.50$; an E-map was computed using the set of signs with the highest figures of merit, revealing the positions of the five Mo and two P atoms. Five cycles of least-squares refinement followed by a difference Fourier map gave the positions of the remaining non-hydrogen atoms. Five more cycles of refinement, assigning anisotropic thermal parameters to the five Mo atoms and isotropic thermal parameters to the remaining atoms, resulted in final values of $R_1=0.047$ and $R_2=0.070$,

with a standard deviation in an observation of unit weight of 1.91.

A final difference Fourier map showed only one peak above $1.0e/Å^3$. This peak of $1.9e/Å^3$ corresponds to about 30% of the electron density found for solvent water, and may be due to some disorder of the molecules of hydration. Some attempts to refine a possible disordered model were made, but the results were not significant.

The final positional and thermal parameters, along with the corresponding standard deviations, are presented in Table III. A table of the final values of $|F_o|$ and $|F_c|$ is available.[6]

TABLE III

Final Positional and Thermal Parameters for $Na[N(CH_3)_4][NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$ (II)

Atom	Fractional coordinates x	y	z	Anisotropic temperature factors ($\times 10^4$)[a] β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.24564(8)	0.22407(4)	0.23308(6)	32.7(8)	9.5(3)	19.6(5)	-2.8(4)	4.6(5)	1.1(3)
Mo(2)	-0.07430(8)	0.21127(4)	0.23012(6)	32.0(8)	9.0(2)	17.5(5)	0.6(4)	5.6(5)	1.2(3)
Mo(3)	-0.12791(8)	0.05044(4)	0.28011(6)	35.7(8)	10.1(3)	20.6(5)	-4.4(4)	5.2(5)	0.7(3)
Mo(4)	0.11935(8)	-0.03873(4)	0.26704(6)	41.8(9)	8.8(3)	18.7(5)	-0.9(4)	2.2(5)	0.9(3)
Mo(5)	0.34086(8)	0.06588(5)	0.22484(6)	33.6(8)	11.0(3)	22.2(5)	0.8(4)	6.2(5)	0.7(3)

Atom	Fractional coordinates x	y	z	Isotropic thermal parameter ($Å^2$) B
P(1)	0.0668(2)	0.0989(1)	0.1165(2)	1.41(5)
P(2)	0.1351(2)	0.1173(1)	0.3804(2)	1.49(5)
Na	0.4929(5)	0.4296(3)	0.0870(4)	4.1(1)
O(1)	0.2708(7)	0.2456(4)	0.1190(5)	2.7(1)
O(2)	0.3018(6)	0.2898(2)	0.2991(5)	2.6(1)
O(3)	0.0811(6)	0.2431(3)	0.2277(4)	1.9(1)
O(4)	0.1972(6)	0.1835(3)	0.3780(5)	1.9(1)
O(5)	0.3645(6)	0.1584(3)	0.2623(5)	2.1(1)
O(6)	0.1827(6)	0.1224(3)	0.1713(4)	1.7(1)
O(7)	0.0133(6)	0.1240(3)	0.3243(4)	1.7(1)
O(8)	-0.0155(6)	0.1574(3)	0.1009(5)	1.9(1)
O(9)	-0.1542(6)	0.2624(3)	0.1514(5)	2.2(1)
O(10)	-0.1043(6)	0.2415(3)	0.3409(5)	2.4(1)
O(11)	-0.1734(6)	0.1342(3)	0.2218(5)	2.1(1)
O(12)	-0.1963(7)	0.0585(3)	0.3826(5)	2.7(1)
O(13)	0.0127(5)	0.0418(3)	0.1679(5)	1.8(1)
O(14)	-0.0100(6)	-0.0105(3)	0.3306(5)	2.0(1)
O(15)	-0.2175(7)	-0.0007(4)	0.2106(5)	2.8(2)
O(16)	0.1951(6)	-0.0812(4)	0.3579(5)	2.6(1)
O(17)	0.2049(6)	0.0590(3)	0.3422(4)	1.8(1)
O(18)	0.2386(6)	-0.0100(3)	0.1932(5)	2.2(1)
O(19)	0.0578(7)	-0.0996(4)	0.1950(5)	2.9(2)
O(20)	0.4033(7)	0.0667(4)	0.1183(5)	3.2(2)
O(21)	0.4410(7)	0.0283(4)	0.3044(5)	3.1(2)
N(1)	0.0949(8)	0.1824(4)	-0.0761(6)	2.8(2)
N(2)	-0.0777(8)	0.1585(4)	0.5095(6)	2.6(2)
N(3)	0.6233(8)	0.3642(5)	0.4755(7)	3.3(2)
C(1)	0.1063(9)	0.0699(5)	0.0025(7)	2.0(2)
C(2)	0.1736(10)	0.1222(5)	-0.0510(7)	2.3(2)
C(3)	0.1119(9)	0.0979(5)	0.5011(7)	2.3(2)
C(4)	0.0460(10)	0.1503(6)	0.5533(8)	2.6(2)
C(5)	0.7247(15)	0.3354(8)	0.4295(12)	6.3(4)
C(6)	0.5216(15)	0.3818(8)	0.4011(11)	6.0(4)
C(7)	0.6628(12)	0.4266(7)	0.5279(10)	4.4(3)
C(8)	0.5878(14)	0.3146(8)	0.5459(11)	5.7(4)
Aq(1)	0.6347(7)	0.4915(4)	0.0015(5)	3.2(2)
Aq(2)	0.3465(8)	0.4077(4)	0.1889(6)	4.5(2)
Aq(3)	0.6063(9)	0.3402(5)	0.1717(7)	5.8(2)
Aq(4)	0.4201(9)	0.3334(5)	-0.0106(7)	5.3(2)
Aq(5)	0.5927(11)	0.2122(7)	0.2776(9)	8.0(3)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

Description of the Structures and Discussion

$(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$(I). The crystal structure of I contains two crystallographically independent, essentially identical $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions (anion I and anion I′), nearly separated by a translation of $\frac{1}{2}$, 0, $\frac{1}{2}$. The two anions are rotated about the Mo_5 ring axis relative to one another. The anions are chiral, and both possess the same handedness to give an optically pure crystal. The NH_4^+ cations and water molecules are in two independent chains, again separated by the $\frac{1}{2}$, 0, $\frac{1}{2}$ translation, running parallel to the b-axis. Figure 1 presents a stereoscopic view of the contents of the unit cell.

All intermolecular contacts are normal, with the shortest NH_4^+ - NH_4^+ distance being 3.89(1)Å between N(5) and N(7). There are no anion-anion contacts less than 3Å, with the closest approach distances being 3.01(1) and 3.05(1)Å for O(10)–O(9′) and O(2′)–O(19′), respectively. (The primed atoms comprise anion I′, and are chemically equivalent to the unprimed atoms of the same number in anion I.)

There appear to be no abnormally short hydrogen-bonded distances, either within the NH_4^+-water molecule chains or between these chains and the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions. Within the chains, the N-Aq distances vary between 2.73 and 2.91Å, while the Aq-Aq distances vary from 2.72 to 3.11Å. The shortest cation-anion and water-anion distances are 2.78(1)Å for N(3)-O(18) and 2.75(1)Å for Aq(6)–O(1′), respectively.

$Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$ (II). The crystal structure of II contains $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ anions, $N(CH_3)_4^+$ cations, and $[Na_2(H_2O)_8]^{2+}$ cations. This is the first example of a zwitterionic heteropoly anion. A stereoscopic view of the unit cell is presented in Figure 2. It can be seen that the $[Na_2(H_2O)_8]^{2+}$ ion, which is located on a center of symmetry, consists of two octahedra joined on one edge by sharing two water molecules. The sixth coordination site of each Na atom is occupied by a terminal oxygen atom (O(21)) of the anion, resulting in dimeric units of two anions linked by the $[Na_2(H_2O)_8]^{2+}$ cation. There is, in addition, one water molecule (Aq(5)) that is not coordinated to the sodium ion but occupies a hole in the packing structure.

All intermolecular contacts are normal, with the closest approach of anions being 3.19Å between O(9) and O(16). The shortest water-anion distance is 2.83Å between Aq(2) and O(15) and between Aq(5) and O(5), while the shortest water-water contact is 2.99Å between Aq(3) and Aq(5). The distances between the positively charged NH_3^+ groups of the anion and the anion oxygens are expectedly shorter, with the closest approaches being 2.77Å between N(2) and O(9) and 2.86Å between N(1) and O(19).

Bond lengths and angles involving the two types of cations are given in Table IV. The $N(CH_3)_4^+$ group has the usual tetrahedral geometry, with C-N-C angles ranging from 107 to 112(1)°

TABLE IV

Selected Distances (Å) and Angles (Deg) for the Cations in

$Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$ (II)

$[N(CH_3)_4]^+$

Atoms	Distance	Atoms	Angle
N(3)-C(5)	1.50(2)	C(5)-N(3)-C(6)	112(1)
N(3)-C(6)	1.54(2)	C(5)-N(3)-C(7)	109(1)
N(3)-C(7)	1.51(2)	C(5)-N(3)-C(8)	107(1)
N(3)-C(8)	1.49(2)	C(6)-N(3)-C(7)	109(1)
		C(6)-N(3)-C(8)	112(1)
		C(7)-N(3)-C(8)	109(1)

$[Na_2(H_2O)_8]^{2+}$

Atoms	Distance	Atoms	Angle
Na-Aq(1)	2.457(10)	Aq(1)-Na-Aq(2)	160.0(4)
Na-Aq(2)	2.355(11)	Aq(1)-Na-Aq(3)	105.2(4)
Na-Aq(3)	2.468(11)	Aq(1)-Na-Aq(4)	109.3(3)
Na-Aq(4)	2.479(11)	Aq(1)-Na-Aq(1)[a]	79.3(3)
Na-Aq(1)[a]	2.431(9)	Aq(1)-Na-O(21)	74.2(3)
Na-O(21)	2.582(9)	Aq(2)-Na-Aq(3)	86.8(4)
		Aq(2)-Na-Aq(4)	88.2(4)
		Aq(2)-Na-Aq(1)[a]	90.2(3)
		Aq(2)-Na-O(21)	88.3(3)
		Aq(3)-Na-Aq(4)	80.5(4)
		Aq(3)-Na-Aq(1)[a]	173.7(4)
		Aq(3)-Na-O(21)	99.2(3)
		Aq(4)-Na-Aq(1)[a]	93.9(3)
		Aq(4)-Na-O(21)	176.5(4)
		Aq(1)[a]-Na-O(21)	86.2(3)

[a]Symmetrically related to Aq(1) by the center of inversion.

and C-N distances ranging from 1.49 to 1.54(2)Å. The coordination geometry about the sodium ion is that of a distorted octahedron, with sodium ion-water distances ranging from 2.36 to 2.48(1)Å and the sodium ion-anion oxygen distance, Na-O(21), being 2.58(1)Å. The Na-Na separation is 3.76(1)Å.

Geometry of the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions (anion I and anion I′) and the $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ anion (anion II). The anions I, I′, and II all possess the same basic structure, as seen in Figure 3 (anion I) and Figure 4 (anion II). The chemically equivalent molybdenum, phosphorus, and oxygen atoms in each anion have been numbered correspondingly. The geometry of each anion is similar to that reported for the $[P_2Mo_5O_{23}]^{6-}$ anion,[7] with a methyl or ethylammonium group replacing the terminal oxygens on phosphorus. Anions I and I′ nearly possess a 2-fold rotation axis running through Mo(4) and O(3), and in anion II this 2-fold symmetry is broken only by the ethylammonium groups. The anions can be considered to be composed of MoO_6 octahedra joined by sharing edges, except for Mo(1) and Mo(2) which share only a corner (Figure 5). Each face of the Mo_5 ring is capped by the tetrahedral RPO_3 groups, with two oxygens atoms each shared by two MoO_6 octahedra and one oxygen atom shared by only one octahedron (Mo(1) or Mo (2)). This results in the asymmetry of the Mo_5 ring previously noted (ref. 7). Selected distances and angles are presented in

Table V. The Mo(1)-Mo(2) distances range from 3.689-3.707(1)Å (avg. 3.696Å) for the three anions (corner-shared MoO_6), while the remaining Mo-Mo distances range from 3.358-3.403(1)Å (avg. 3.383Å) for the edge-shared octahedra.

The P-C distances in anions I, I′, and II and the C-C and C-N distances in anion II also appear normal. The P-C bond lengths range from 1.78-1.81(1)Å (avg. 1.796Å), while in anion II the C-C distances are 1.55(2) and 1.53(2)Å and the C-N distances are 1.54(1) and 1.51(1)Å. The P-C-C and C-C-N angles range from 110-116(1)°.

The Mo-O and P-O bond lengths are consistent with those previously reported,[7] with average distances and ranges given in Table VI. It can be seen that the Mo-O distance increases considerably as the sharing of oxygen atoms increases, with average values of 1.71Å for terminal Mo-O bonds to 2.33Å for Mo-O bonds in which the oxygen atom is shared by two Mo atoms and one P atom. The increase in P-O bond lengths is not nearly so marked, with average values of 1.52Å for P-O bonds in which the oxygen atom is shared by one P atom and one Mo atom to 1.54Å for Mo-O bonds with the oxygen atom shared by one P atom and two Mo atoms. These distances can be compared to the average values for P-O bond lengths of 1.50, 1.52, and 1.56(1) Å reported for terminal, doubly-shared, and triply-shared oxygen atoms, respectively, in the $[P_2Mo_5O_{23}]^{6-}$ anion.[7] Table V also

TABLE V

Selected Distances (Å) and Angles (Deg) for the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ (I and I′) and $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ (II) Anions

Mo-Mo, P-Mo and P-P Distances

Atoms	Distance		
	Anion I	Anion I′	Anion II
Mo(1)-Mo(2)	3.693(1)	3.707(1)	3.689(2)
Mo(2)-Mo(3)	3.375(1)	3.394(1)	3.385(1)
Mo(3)-Mo(4)	3.368(1)	3.358(1)	3.385(1)
Mo(4)-Mo(5)	3.394(1)	3.388(1)	3.403(2)
Mo(5)-Mo(1)	3.382(1)	3.384(1)	3.376(2)
P(1)-Mo(1)	3.616(3)	3.269(2)	3.561(3)
P(1)-Mo(2)	3.302(2)	3.296(2)	3.288(3)
P(1)-Mo(3)	3.529(2)	3.562(2)	3.501(3)
P(1)-Mo(4)	3.470(3)	3.444(2)	3.512(3)
P(1)-Mo(5)	3.440(3)	3.431(2)	3.442(3)
P(2)-Mo(1)	3.330(2)	3.295(3)	3.325(3)
P(2)-Mo(2)	3.628(2)	3.621(3)	3.600(3)
P(2)-Mo(3)	3.467(3)	3.448(3)	3.492(3)
P(2)-Mo(4)	3.433(3)	3.443(2)	3.523(3)
P(2)-Mo(5)	3.551(2)	3.589(3)	3.529(3)
P(1)-P(2)	3.776(3)	3.772(3)	3.753(4)

Mo-O and P-O Distances

	Atoms	Distance		
		Anion I	Anion I′	Anion II
Terminal oxygen	Mo(1)-O(1)	1.722(6)	1.717(7)	1.717(7)
	Mo(1)-O(2)	1.694(7)	1.694(6)	1.712(7)
	Mo(2)-O(9)	1.683(6)	1.699(6)	1.718(7)
	Mo(2)-O(10)	1.733(6)	1.716(6)	1.741(7)
	Mo(3)-O(12)	1.720(6)	1.695(7)	1.716(7)
	Mo(3)-O(15)	1.718(7)	1.720(6)	1.703(7)
	Mo(4)-O(16)	1.705(6)	1.722(6)	1.712(7)
	Mo(4)-O(19)	1.732(7)	1.718(6)	1.705(7)
	Mo(5)-O(20)	1.706(7)	1.683(7)	1.725(8)
	Mo(5)-O(21)	1.698(7)	1.725(7)	1.710(8)
Oxygen doubly shared by two Mo atoms	Mo(1)-O(5)	1.930(6)	1.920(6)	1.921(7)
	Mo(1)-O(3)	1.912(6)	1.926(6)	1.927(7)
	Mo(2)-O(3)	1.921(7)	1.923(6)	1.903(7)
	Mo(2)-O(11)	1.921(7)	1.925(6)	1.924(7)
	Mo(3)-O(11)	1.912(6)	1.946(6)	1.929(7)
	Mo(3)-O(14)	1.940(6)	1.948(6)	1.918(7)
	Mo(4)-O(14)	1.912(6)	1.924(6)	1.895(7)
	Mo(4)-O(18)	1.938(6)	1.909(6)	1.889(7)
	Mo(5)-O(18)	1.934(6)	1.948(6)	1.956(7)
	Mo(5)-O(5)	1.928(6)	1.537(6)	1.950(7)

TABLE V - Continued

	Atoms	Distance Anion I	Distance Anion I'	Distance Anion II
Oxygen doubly shared by one Mo atom and one P atom	Mo(1)-O(4)	2.257(6)	2.233(6)	2.317(7)
	Mo(2)-O(8)	2.242(6)	2.251(6)	2.278(7)
	P(1)-O(8)	1.516(6)	1.537(6)	1.515(7)
	P(2)-O(4)	1.508(6)	1.520(6)	1.516(7)
Oxygen triply shared by two Mo atoms and one P atom	Mo(1)-O(6)	2.382(6)	2.398(5)	2.316(6)
	Mo(2)-O(7)	2.423(6)	2.387(6)	2.372(6)
	Mo(3)-O(7)	2.240(7)	2.225(6)	2.246(7)
	Mo(3)-O(13)	2.369(6)	2.374(6)	2.373(7)
	Mo(4)-O(13)	2.313(6)	2.303(6)	2.404(7)
	Mo(4)-O(17)	2.288(6)	2.294(6)	2.404(7)
	Mo(5)-O(17)	2.384(6)	2.440(7)	2.385(7)
	Mo(5)-O(6)	2.207(6)	2.220(6)	2.221(7)
	P(1)-O(6)	1.560(6)	1.542(6)	1.553(7)
	P(1)-O(13)	1.535(7)	1.534(6)	1.524(7)
	P(2)-O(7)	1.529(7)	1.558(6)	1.552(7)
	P(2)-O(17)	1.543(6)	1.525(6)	1.547(7)

Additional Distances

I

Atoms	Distance
P(1)-C(1)	1.790(10)
P(1')-C(1')	1.802(10)
P(2)-C(2)	1.784(9)
P(2')-C(2')	1.802(10)

II

Atoms	Distance
P(1)-C(1)	1.808(10)
P(2)-C(3)	1.791(10)
C(1)-C(2)	1.546(15)
C(3)-C(4)	1.527(15)
C(2)-N(1)	1.537(14)
C(2)-N(2)	1.509(14)

Angles about Mo

Atoms	Angle Anion I	Angle Anion I'	Angle Anion II
O(1)-Mo(1)-O(2)	101.8(3)	101.7(3)	103.1(3)
O(1)-Mo(1)-O(3)	97.6(3)	96.9(3)	99.4(3)
O(1)-Mo(1)-O(4)	172.1(3)	172.6(3)	172.4(3)
O(1)-Mo(1)-O(5)	102.1(3)	100.9(3)	101.4(3)
O(1)-Mo(1)-O(6)	85.3(3)	84.5(3)	86.8(3)
O(2)-Mo(1)-O(3)	103.2(3)	103.9(3)	100.9(3)
O(2)-Mo(1)-O(4)	86.0(3)	85.4(3)	84.4(3)
O(2)-Mo(1)-O(5)	100.2(3)	100.4(3)	100.9(3)
O(2)-Mo(1)-O(6)	168.4(3)	169.1(3)	168.1(3)

TABLE V - Continued

Atoms	Angle Anion I	Angle Anion I'	Angle Anion II
O(3)-Mo(1)-O(4)	79.4(2)	79.6(2)	77.8(3)
O(3)-Mo(1)-O(5)	145.5(3)	146.1(2)	145.4(3)
O(3)-Mo(1)-O(6)	84.8(2)	84.0(2)	83.6(3)
O(4)-Mo(1)-O(5)	77.2(2)	79.2(2)	78.0(3)
O(4)-Mo(1)-O(6)	87.2(2)	88,7(2)	85.8(2)
O(5)-Mo(1)-O(6)	69.1(2)	69.4(2)	70.4(3)
O(3)-Mo(2)-O(7)	84.3(2)	84.0(2)	84.7(3)
O(3)-Mo(2)-O(8)	80.3(2)	80.0(2)	78.3(3)
O(3)-Mo(2)-O(9)	102.0(3)	102.5(3)	103.6(3)
O(3)-Mo(2)-O(10)	99.8(3)	98.0(3)	99.3(3)
O(3)-Mo(2)-O(11)	145.2(2)	145.5(2)	145.5(3)
O(7)-Mo(2)-O(8)	88.2(2)	89.7(2)	87.3(2)
O(7)-Mo(2)-O(9)	171.0(3)	170.4(3)	168.8(3)
O(7)-Mo(2)-O(10)	83.4(3)	84.2(3)	82.3(3)
O(7)-Mo(2)-O(11)	69.6(2)	69.5(2)	69.9(3)
O(8)-Mo(2)-O(9)	86.5(3)	84.5(3)	87.1(3)
O(8)-Mo(2)-O(10)	171.6(3)	173.7(3)	169.5(3)
O(8)-Mo(2)-O(11)	76.4(2)	78.2(2)	77.6(3)
O(9)-Mo(2)-O(10)	101.7(3)	101.8(3)	103.4(3)
O(9)-Mo(2)-O(11)	102.0(3)	101.7(3)	99.4(3)
O(10)-Mo(2)-O(11)	99.7(3)	100.8(3)	99.9(3)
O(7)-Mo(3)-O(11)	74.0(2)	72.9(2)	72.7(3)
O(7)-Mo(3)-O(12)	96.2(3)	96.8(3)	94.6(3)
O(7)-Mo(3)-O(13)	73.0(2)	72.6(2)	73.3(2)
O(7)-Mo(3)-O(14)	80.9(2)	81.2(2)	81.3(3)
O(7)-Mo(3)-O(15)	160.0(3)	159.2(3)	160.7(3)
O(11)-Mo(3)-O(12)	99.8(3)	99.1(3)	98.6(3)
O(11)-Mo(3)-O(13)	86.9(2)	85.5(2)	87.4(3)
O(11)-Mo(3)-O(14)	151.1(3)	150.2(3)	150.9(3)
O(11)-Mo(3)-O(15)	98.7(3)	98.0(3)	99.0(3)
O(12)-Mo(3)-O(13)	165.3(3)	166.7(3)	164.4(3)
O(12)-Mo(3)-O(14)	96.8(3)	98.3(3)	96.4(3)
O(12)-Mo(3)-O(15)	103.4(3)	103.2(4)	104.0(4)
O(13)-Mo(3)-O(14)	72.1(2)	72.7(2)	72.4(3)
O(13)-Mo(3)-O(15)	88.2(3)	88.3(3)	89.2(3)
O(14)-Mo(3)-O(15)	100.1(3)	101.3(3)	101.4(3)
O(13)-Mo(4)-O(14)	73.9(2)	74.8(2)	72.0(2)
O(13)-Mo(4)-O(16)	169.1(3)	167.6(3)	166.1(3)
O(13)-Mo(4)-O(17)	80.8(2)	80.3(2)	82.6(2)
O(13)-Mo(4)-O(18)	80.6(2)	80.7(2)	80.2(3)
O(13)-Mo(4)-O(19)	87.9(3)	88.2(3)	88.6(3)
O(14)-Mo(4)-O(16)	101.2(3)	96.6(3)	99.4(3)
O(14)-Mo(4)-O(17)	83.3(2)	80.6(2)	81.5(3)
O(14)-Mo(4)-O(18)	147.7(3)	147.7(2)	144.2(3)
O(14)-Mo(4)-O(19)	101.9(3)	102.2(3)	101.4(3)
O(16)-Mo(4)-O(17)	89.1(3)	89.5(3)	85.4(3)
O(16)-Mo(4)-O(18)	100.2(3)	103.7(3)	102.8(3)
O(16)-Mo(4)-O(19)	102.8(3)	102.6(3)	104.0(3)
O(17)-Mo(4)-O(18)	73.2(2)	74.8(2)	72.7(3)
O(17)-Mo(4)-O(19)	165.7(3)	167.0(3)	169.5(3)

TABLE V - Continued

Atoms	Angle Anion I	Anion I'	Anion II
O(18)-Mo(4)-O(19)	96.6(3)	97.6(3)	100.1(3)
O(5)-Mo(5)-O(6)	73.1(2)	73.2(2)	72.1(3)
O(5)-Mo(5)-O(17)	87.7(2)	86.6(2)	87.2(3)
O(5)-Mo(5)-O(18)	151.1(3)	149.7(3)	151.1(3)
O(5)-Mo(5)-O(20)	99.5(3)	100.7(3)	99.7(3)
O(5)-Mo(5)-O(21)	97.4(3)	98.4(3)	100.1(3)
O(6)-Mo(5)-O(17)	73.3(2)	72.3(2)	72.3(2)
O(6)-Mo(5)-O(18)	82.0(2)	80.9(2)	82.2(3)
O(6)-Mo(5)-O(20)	96.4(3)	96.6(3)	95.3(3)
O(6)-Mo(5)-O(21)	158.1(3)	159.3(3)	158.8(3)
O(17)-Mo(5)-O(18)	71.0(2)	70.7(2)	72.1(3)
O(17)-Mo(5)-O(20)	165.3(3)	164.6(3)	163.4(3)
O(17)-Mo(5)-O(21)	86.8(3)	88.6(3)	88.0(3)
O(18)-Mo(5)-O(20)	97.6(3)	97.5(3)	95.6(3)
O(18)-Mo(5)-O(21)	100.6(3)	100.6(3)	99.2(3)
O(20)-Mo(5)-O(21)	104.8(3)	103.6(4)	105.4(4)

Angles about P

Atoms	Angle Anion I	Anion I'	Anion II
O(6)-P(1)-O(8)	109.6(3)	108.5(3)	109.5(4)
O(6)-P(1)-O(13)	110.7(3)	110.8(3)	111.3(4)
O(6)-P(1)-C(1)	106.7(4)	108.8(4)	105.5(4)
O(8)-P(1)-O(13)	110.6(3)	111.7(4)	112.3(4)
O(8)-P(1)-C(1)	111.1(4)	109.3(4)	109.0(4)
O(13)-P(1)-C(1)	108.1(5)	107.6(4)	109.0(4)
O(4)-P(2)-O(7)	109.3(3)	109.8(3)	108.5(4)
O(4)-P(2)-O(17)	110.1(3)	111.0(4)	113.5(4)
O(4)-P(2)-C(2)[a]	108.5(4)	108.1(4)	109.0(4)
O(7)-P(2)-O(17)	110.7(3)	110.8(3)	111.3(4)
O(7)-P(2)-C(2)[a]	109.2(4)	108.5(4)	107.3(4)
O(17)-P(2)-C(2)[a]	109.0(4)	108.5(4)	107.1(4)

Angles about C

Atoms	Angle (Anion II)
P(1)-C(1)-C(2)	113.1(7)
P(2)-C(3)-C(4)	115.6(8)
C(1)-C(2)-N(1)	109.9(8)
C(3)-C(4)-N(2)	111.8(9)

[a]Corresponds to C(3) in Anion II.

TABLE VI

Average Mo-O and P-O Bond Distances (Å)

Atoms	Number Averaged	Type of Oxygen Atom	Range	Average
Mo-O	30	Terminal	1.683-1.741[a]	1.712
Mo-O	30	Doubly shared by two Mo atoms	1.889-1.956	1.926
Mo-O	6	Doubly shared by one Mo atom and one P atom	2.233-2.317	2.263
Mo-O	24	Triply shared by two Mo atoms and one P atom	2.207-2.440	2.332
P-O	6	Doubly shared by one P atom and one Mo atom	1.508-1.537	1.519
P-O	12	Triply shared by one P atom and two Mo atoms	1.524-1.560	1.542

[a]Average estimated standard deviations are 0.006 Å for Mo-O and 0.007 Å for P-O.

shows that, whereas the MoO_6 octahedra exhibit large angular variations from the ideal octahedral geometry, the RPO_3 tetrahedral angles remain close to the predicted value, ranging from 106 to 112°. Thus it appears that the organophosphonate portion of the anion retains its original structure insofar as possible, while the MoO_6 octahedra are considerably distorted in forming the heteropoly anion. This retention of geometry by the phosphate or organophosphonate moiety might account for the inability to isolate the corresponding As_2Mo_5 ions[8], with arsenic in place of phosphorus. The larger covalent radius of arsenic (1.22Å *vs.* 1.10Å for phosphorus[9]) might sterically inhibit the formation of heteropoly ions of this type with molybdenum.

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References

1. W. Kwak, M.T. Pope, and T.F. Scully, J.Amer.Chem.Soc., in press.
2. See, for example, the structure of $[C(NH_2)_3]_2[(CH_3)_2AsMo_4O_{14}(OH)]$, K.M. Barkigia and C.O. Quicksall, Abstracts, 25th Anniversary Meeting of the American Crystallographic Association, Charlottesville, Va., No. J19.
3. Programs used for the structure solutions and refinements included local modifications of the ALFF Fourier program by Hubbard, Quicksall, and Jacobson, the Busing-Levy ORFLS least-squares and ORFFE error function programs, Johnson's ORTEP plotting program, and the LSAM series by Main, Woolfson, and Germain.
4. H.P. Hanson, F. Herman, J.D. Lea, and S. Skillman, Acta Crystallogr., 17, 1040 (1964).
5. D.T. Cromer, Acta Crystallogr., 18, 17 (1965).
6. Supplementary material.
7. R. Strandberg, Acta Chem. Scand., 27, 1004 (1973).
8. M.T. Pope and W. Kwak, private communication.
9. J.E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity," Harper and Row, New York, N.Y., 1972, Table 5.1.

Captions for Figures

Figure 1. A stereoscopic view of the unit cell of $(NH_4)_4[(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$ ($\underset{\sim}{I}$). The anions show MoO_6 octahedra; all other vibrational ellipsoids are drawn at the 50% probability level. In the H_2O - NH_4^+ chains the probable N atoms have been shaded.

Figure 2. A stereoscopic view of the unit cell of $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H_2O$ ($\underset{\sim}{II}$). The anions show MoO_6 octahedra; all other vibrational ellipsoids are drawn at the 50% probability level. The Na atoms of the $[Na_2(H_2O)_8]^{2+}$ cations have been shaded.

Figure 3. A stereoscopic view of the $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anion (anion $\underset{\sim}{I}$), with vibrational ellipsoids drawn at the 50% probability level.

Figure 4. A stereoscopic view of the $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ anion (anion $\underset{\sim}{II}$). The vibrational ellipsoids are drawn at the 50% probability level.

Figure 5. The $[(NH_3C_2H_4P)_2Mo_5O_{21}]^{2-}$ anion (anion $\underset{\sim}{II}$) showing the MoO_6 octahedra.

Fig. 1

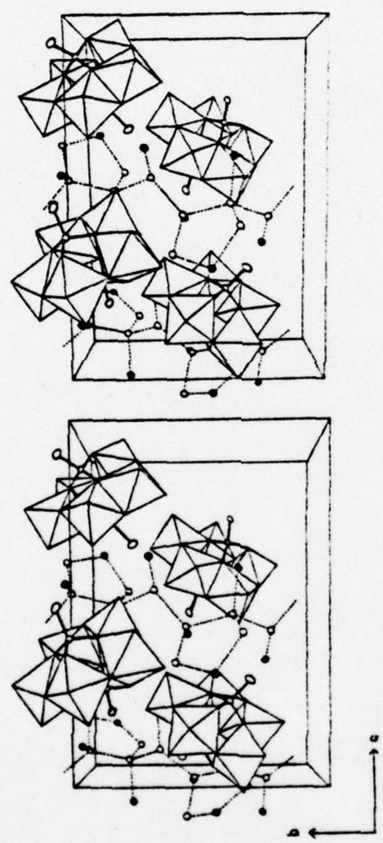


Fig. 2

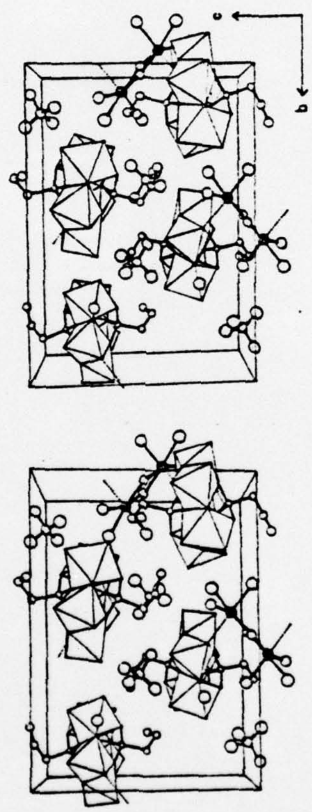


Fig. 3

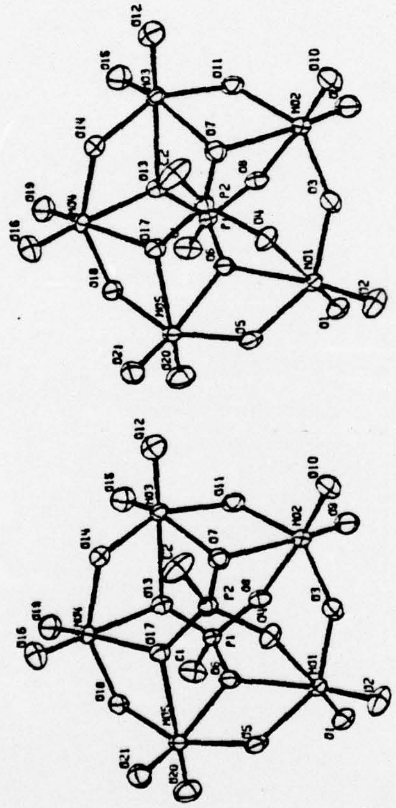


Fig 4

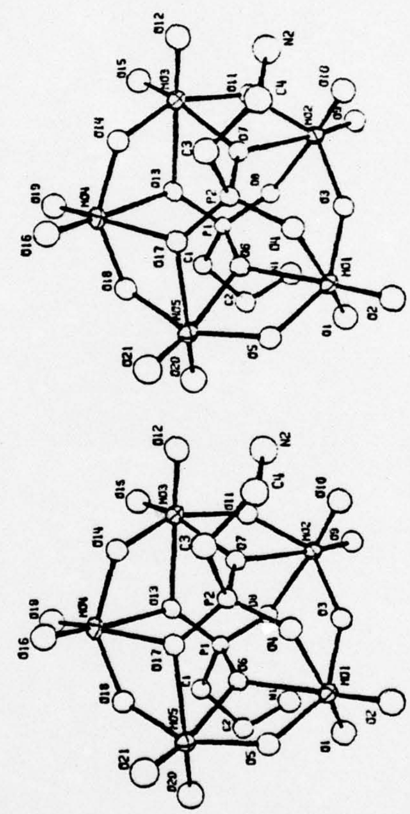
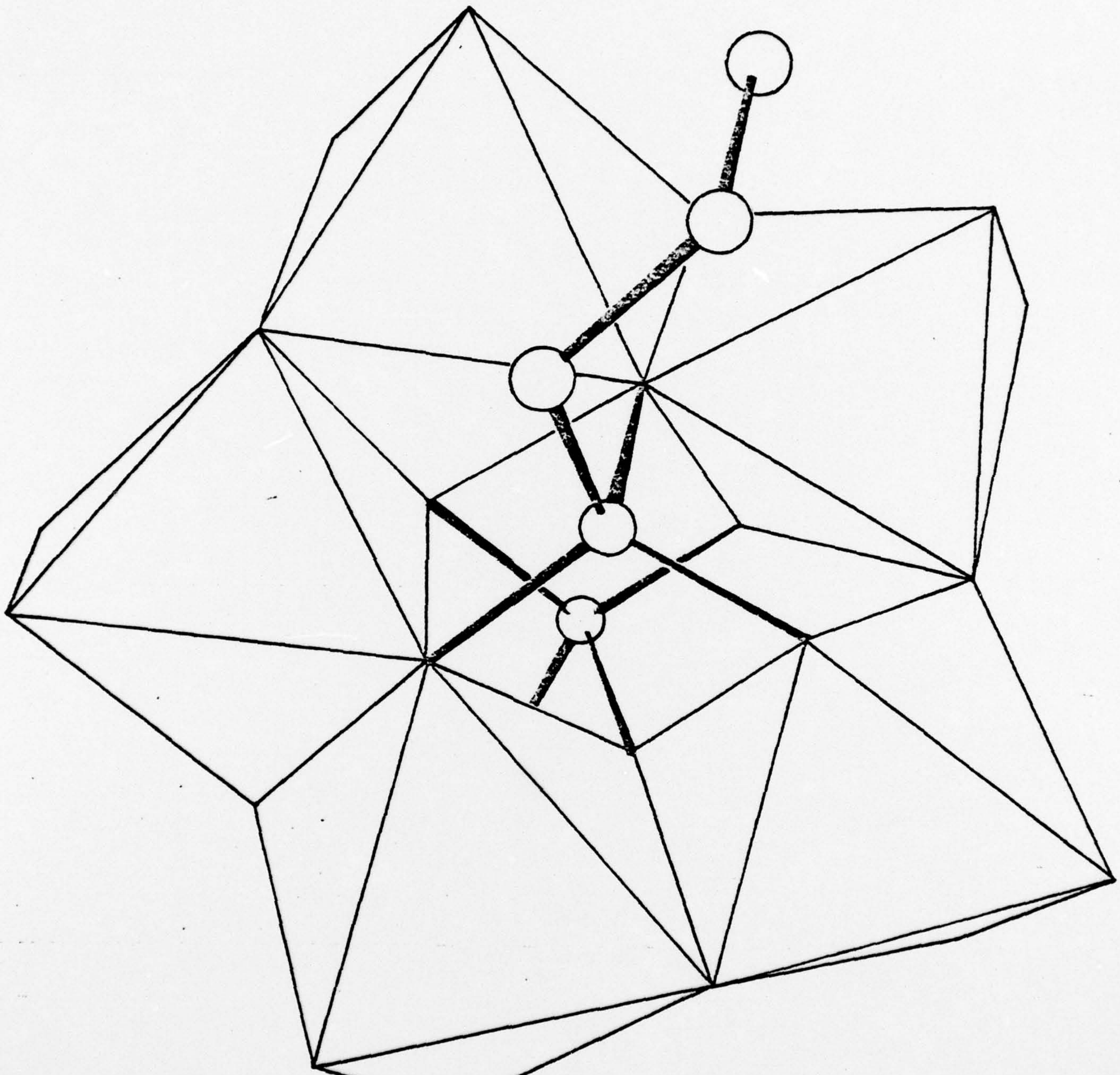


Fig 5



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13. ABSTRACT

The crystal and molecular structures of two stable organic derivatives of a heteropoly anion have been determined from three-dimensional X-ray data collected by counter methods. The pentamolybdomethylphosphonate compound, $(NH_4)_4 - [(CH_3P)_2Mo_5O_{21}]\cdot 5H_2O$, crystallizes in space group $C_2{}^2$-$P2_1$ of the monoclinic system with four formula units in a cell of dimensions a=10.597(2), b=13.739(2), c=19.901(2)Å; =96.05(1)°. The observed and calculated densities are 2.48(2) and 2.466 g/cm^3, respectively. The pentamolybdoethylammoniumphosphonate compound, $Na[N(CH_3)_4][(NH_3C_2H_4P)_2Mo_5O_{21}]\cdot 5H\ O$, crystallizes in space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system, with four formula units in a cell of dimensions a=11.513(4), b=20.146(6), c=14.110(5)Å; =95.25(4) The observed and calculated densities are 2.36(2) and 2.354 g/cm^3, respectively. Both structures have been refined by least-squares techniques to final R factors on F of 0.032 for the methyl compound and 0.047 for the ethylammonium compount. The structures of both organoheteropoly anions are similar, consisting of rings of five MoO_6 octrahedra corner-sharing. Each face of the Mo_5 ring is capped by a tetrahedral RPO_3 group ($R=CH_3$ or $C_2H_4NH_3{}^+$). The crystal structure of the methyl compound contains contains two independent $[(CH_3P)_2Mo_5O_{21}]^{4-}$ anions of the same chirality related by a pseudo-symmetric B-centering. The ammonium ions and water molecules form infinite hydrogen-bonded chains parallel to the b axis. In the ethylammonium crystal the

$[(NH_3C_2H_5P)_2Mo_5O_{21}]^{2-}$ anions are loosely linked together as dimers by sodium ion - oxygen coordination. This is the first example of a zwitterionic heteropoly anion.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Heteropoly complexes Organic derivatives Crystal structures Molybdophosphonates						